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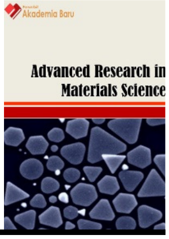

Effect of Noble Metal Thin Film Thicknesses on Surface Plasmon Resonance (SPR) Signal Amplification

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ABSTRACT

This work is carried out to study the effect of noble metal thicknesses, namely gold and silver on the SPR characteristics for smart food packaging technology applications. A Kretschmann prism coupling was introduced to excite surface plasmon polaritons (SPP). The optical refractive indices values of gold and silver were set as Rgold=0.1759+3.4104i and Rsilver=0.0585+4.2665i respectively. The thicknesses of noble metal thin films were varied between t=25nm and 95nm with the increment of 10nm for each reading. SPR signal analyses were performed by studying the characteristics of SPR peaks such as Q-factor and FWHM. Both analyses demonstrated an outstanding optical properties of silver at t=55nm in comparison with gold due to its low FWHM and high Q-factor values which proves its ability to generate excellent amount of SPP. The employment of silver witnessed the enhancement of Q-factor value up to 7.09% and the decrement of FWHM about 76.58%, relatively with gold. The introduction of silver able to convert 87.20% SPP, whilst the usage of gold only capable to excite 81.4% SPP. In conclusion, application of silver noble metal at t=55nm able to generate maximum SPR. This excellent criterion placed silver as a spectacular candidate in the development of low cost and high sensitive SPR sensor for food quality assessment applications.

Keywords:
Surface Plasmon Resonance (SPR), noble metals, FWHM, Q-factor, smart food packaging

1. Introduction

The needs of safe foods by ensuring their freshness have led to the introduction of smart food packaging technology which capable to observe the food quality and manage product authenticity [1,2]. Food packaging is very important to protect food from environmental that causes the quality

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degradation of food or drink due to moisture and microbes [3]. Poor packaging will expose the consumers on dangerous health risks such as food poisoning which is caused by the rapid growth of bacteria in these products that possibly stemmed the excretion of nitrogen and sulfur containing compound [4]. Due to the awareness on food safety, a smart packaging technology has been introduced to our community. Smart packaging indicators able to track interaction between the food, the packaging, and the environment [5]. These systems provide better advantageous than the conventional one such as able to monitor product quality and trace the threshold of food safety level. Today, there are two types of smart indicator which have been initiated such as indirect indicator and direct indicator [6]. The indirect indicator is based on polymerization rate and chemical reaction. The direct indicator is more favorable than the previous one due to its high precision ability in detecting the presence of carbon dioxide (CO_2). The role of CO_2 is to avoid or reduce the oxygen content by creating protective atmosphere surrounding the food inside of a pack. Freshness and quality of food can be evaluated by determination of CO_2 concentrations.

By considering the importance of CO_2 detection in food safety, the demands of high sensitivity CO_2 gas sensor become a priority in smart food packaging technology [7]. Recently, various types CO_2 sensors have been employed in food packaging technology which are chemical sensors [8-10], electrochemical sensors [11] and optical sensors [12-14]. Optical sensors are more attractive due to its high sensitivity, better accuracy, less bulky and low cost [15]. Optical sensors typically can be categorized into types, such as fiber optics based (i.e conventional fiber optics and tapered fiber optics) [16-18] and optical free space based [19]. Surface plasmon resonance (SPR) sensor is one of the favorable optical free space based-sensors by considering the simplicity of its structure [20-21]. SPR is a phenomenon where the evanescent field is created by striking the p-polarized incident light onto the metal-coated prism. Its sensing working principle is based on the changes of refractive indices of the sensing medium i.e. CO_2.

One of the main requirements in developing SPR sensor is the presence of noble metal thin film to generate surface plasmon polaritons (SPP). The interaction of metals with electromagnetic wave is mainly influenced by the free conduction electrons in metal. A high reflectance will be occurred at optical frequencies because most metals experience a negative dielectric constant [22]. At these frequencies, the metal's free electron gas can sustain surface and volume charge density oscillations called plasmon polaritons. The surface charge density oscillations identified with surface plasmons at the interface between a metal and a dielectric can give increment to strongly enhanced optical near fields which are spatially confined near the metal surface [22]. Gold nanostructures whether in form of thin films nor nanoparticles; are the most common noble metal employed to excite SPR by considering its high resistance in oxidation issue [23-27]. Due to high cost issue, other noble metal such as silver and platinum become an alternative option to generate SPR [28-29]. Attractively, the employment of alternative noble metals able to excite almost similar percentage of SPP. The thickness of metal films plays a crucial role in the development of high sensitivity SPR sensor. Until now, an ideal thickness of metals to generate maximum SPR is within the range of 40nm to 60nm [30-31].

This work is carried out to study the effect of noble metal thin film thicknesses, namely silver and gold on SPR. The thicknesses for both metals were varied between 25nm until 95nm. We managed to prove that the employment of silver able to generate better SPR intensity than gold. We believe that the output of this work able to contribute to the development of low cost and high sensitive SPR sensor in food safety technology.

2. Methodology

To validate type of light propagation mode, firstly a p-polarized 633nm red laser was incident on the hypothenuse side of the bare prism (RI of prism=1.51). An existence of Brewster angle and critical angle were observed. The presence of Brewster angle indicated the propagation of p-polarized light which is a principal requirement in exciting surface plasmon polaritons (SPP). Location of critical angle is also a crucial indicator since SPR must occur during total internal reflection (TIR). Note that SPR unable to exist below the critical angle by considering that the energy is not sufficient to generate SPP [32].

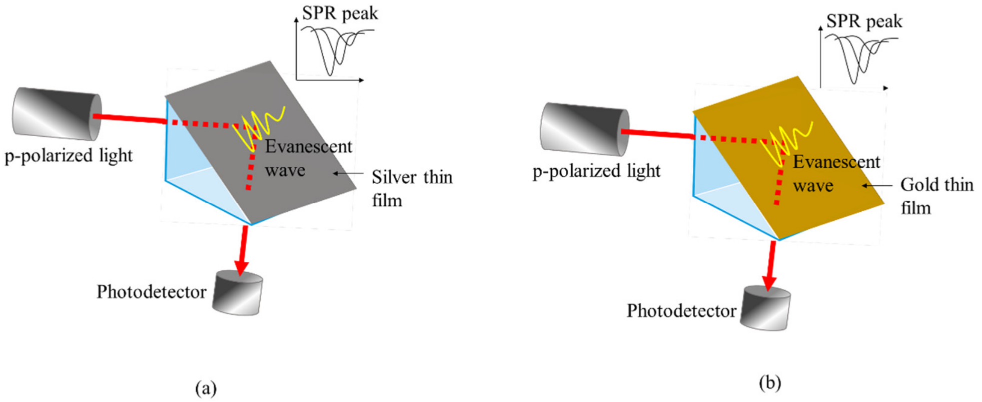


Fig. 1. SPR experimental setup using Kretschmann prism coupling consisted of different types of noble metal thin films (a) silver (b) gold. SPR peaks were shifted with the modulation of thin film thicknesses

Next the experiment was repeated by introduced the same p-polarized laser on the hypothenuse side of noble metal coated triangular prism as illustrated in Fig. 1. Two types of noble metals, namely silver (Fig. 1(a)) and gold (Fig. 1(b)) with refractive indices of 0.0585+4.2665k and 0.1759+3.4104k were employed. The thicknesses of noble metal films were varied between t=25nm and t=95nm with increment of 10nm for each reading. SPR signal was generated by manipulating the laser incident angle from θ_i=40.0° to θ_i=47.0°. The properties of SPR were analyzed by studying the shape of SPR curve such as full-width-half-maximum (FWHM), Q-factor which represent by the SPR curve depth and percentage amount of plasmons excitation. Excellent SPR signal can be identified by a small FWHM and large Q-factor.

3. Results and Discussions

An incident light was well calibrated into p-polarized mode represented by the appearance of Brewster angle at θ_B=30° as illustrated in Figure 2. The location of critical angle was observed at 39.85°. This output suggests that the SPR phenomena should be observed beyond this angle under TIR condition by considering the sufficient amount of energy to excite plasmons. Thickness of metal thin film plays a significant role in developing a high sensitivity SPR sensor as portrays in Figure 3. Deeper SPR curve exhibits strong SPR signal and vice versa [33]. Figure 3(a) shows the generation of SPR by varying thicknesses of silver thin films. At t=25nm, SPR was almost not occurred representing by a very shallow and wide curve. This condition happened due to electron damping oscillation experienced between the dielectric and metal layers [34]. As its thickness increased to t=35nm, value of R_{min} was obtained as 0.388 a.u at incident angle of 42.261°. Value of R_{min} dropped to 0.144 a.u with the increment of thickness to t=45nm. Maximum excitation of SPR was resulted when thickness of silver was set at t=55nm with R_{min}=0.031 a.u at θ_{SPR}= 41.96° representing by a deep and narrow curve. Note that the SPR angles were blue-shifted about 0.301° as thicknesses were raised from t=25nm to t=55nm. Value of R_{min} became greater when the thicknesses were increased beyond t=55nm. At t=65nm, R_{min} was resulted as 0.344 a.u. The strength of SPR signal became weaker at t=75nm where value of R_{min} was obtained as R=0.632 a.u. With the increment of silver thicknesses from t=85nm to t=95nm, SPR signal were less significant resulting the values of R_{min} as 0.781 a.u and 0.848 a.u respectively. It was obviously seen that the SPR angle remained at 41.96° when silver thicknesses were increased from t=55nm to t=95nm. This analysis manifests the stabilization of SPR signal as silver thicknesses were set at t$\geq$55nm. The signal was apparently weak and less stable below t=55nm based on the properties of shallow SPR curve depth and their angle shifting.

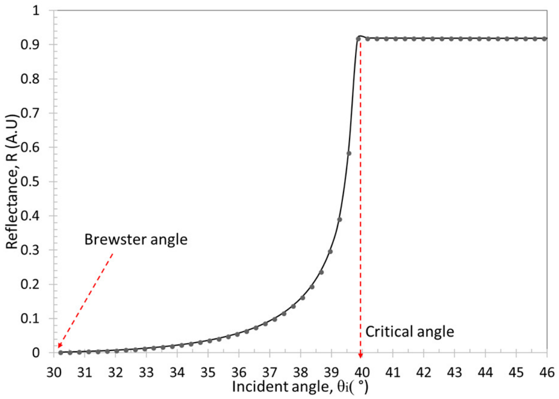
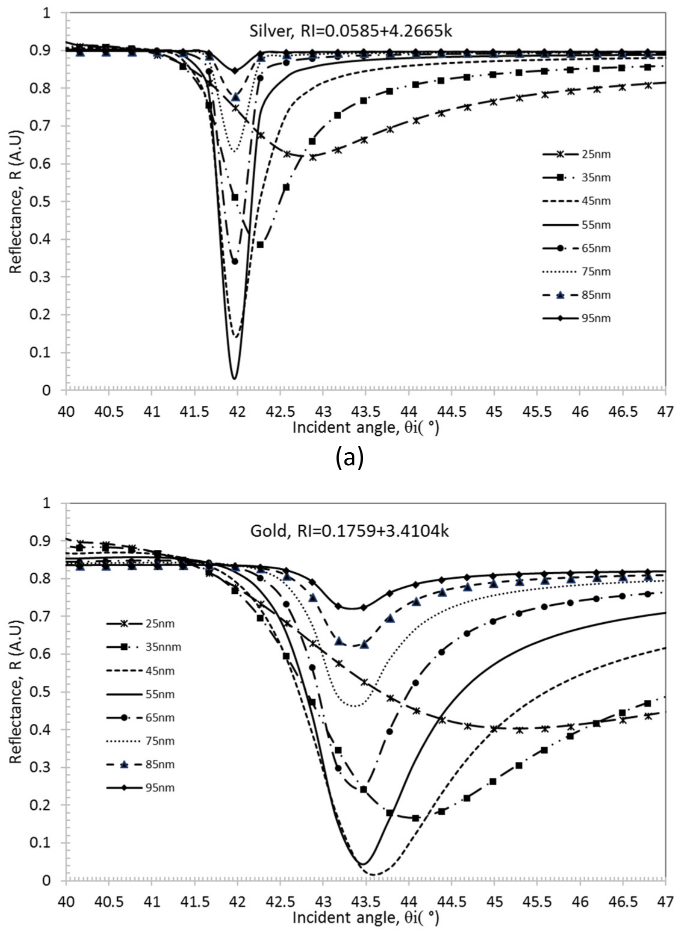


Fig. 2. The presence of Brewster angle, θ_B at 30° and critical angle at θ_c at 39.85°

Figure 3(b) represents the characteristics of SPR as gold thin films were coated on the hypothenuse side of bare prism. Overall, the SPR properties of gold resulted wider curves than silver. This situation demonstrates that gold SPR sensor is less efficient than silver. At t=25nm, the SPR peak was not clearly observed. With the increment of thickness to t=35nm, a wider and shallower SPR peak was slowly observed with R_{min}=0.1661 a.u at 44.07°. The minimum value of R_{min}=0.031 a.u at incident angle of 43.77° was resulted as the thickness was set at t=45nm. Value of R_{min} was increased to 0.043 a.u when thickness of gold was raised at t=55nm. At this respective thickness, the SPR angle experienced 0.30° of blue shifting resulted θ_{SPR}=43.47°. We noticed similar characteristics as silver (Figure 3(a)) , where SPR angle shifting of gold was no more occurred at t$\geq$55nm. Value of R_{min} was steadily increased as gold thicknesses were raised from t=65nm until t=95nm indicated poorer SPR signals. Bear in mind that the value minimum reflectance does not solely represents maximum excitation of plasmons because in some occasions, the maximum reflectance during the critical angle does not achieved R=1 a.u. To avoid this misunderstanding, the Q-factor analysis is more accurate to represents the actual strength of SPR excitation.



(a)

(b)

Fig. 3. SPR curves for several types of noble metals with various thicknesses between 25nm and 95nm (a) silver (b) gold

Figure 4 illustrates the FWHM analysis between silver and gold. Apparently, the SPR properties of silver portrays smaller FWHM than gold due to its deep and narrow peak which proves its ability to generate excellent amount of SPP. This excellent criterion placed silver as a spectacular candidate in the development of high sensitive SPR sensor. In general, both noble metals were exponentially decreased of FWHM with the increment of thicknesses. Largest FWHM were obtained at t=25nm, where gold experienced greater value of FWHM ($FWHM_{gold}$=15.75°) than silver ($FWHM_{silver}$=3.2°). At t=55nm, the FWHM became more stabilize with the average value of 0.336° and 1.222° for silver and gold respectively. This analysis proves that type of noble metals and their thicknesses mainly influenced the properties of the SPR signal.

Figure 5 depicts the Q-factor analysis for gold and silver as their thicknesses were modulated. Note that greater Q-factor exhibits stronger excitation of SPP. It is interesting to observe that the Q-$factor_{gold}$ were greater than Q-$factor_{silver}$ at t=25nm until t=45nm. However, at t=55nm, SPP was excellently excited with the employment of silver where the Q-factor was obtained as 0.872 a.u which is 7.09% greater than gold. As the thicknesses were increased from t=65nm to t=95nm, the SPR excitation became poorer due to the electron absorption by the metal itself. This result demonstrates that the optimum amplification of SPR signal can be achieved by employing silver thin film with thicknesses of 55nm.

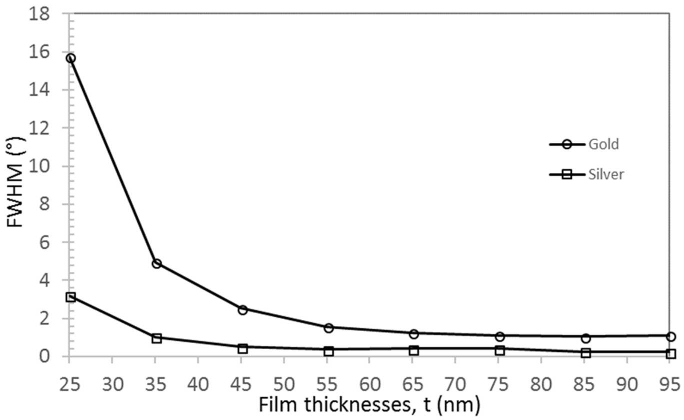


Fig. 4. Analysis of FWHM for silver and gold with numerous thicknesses

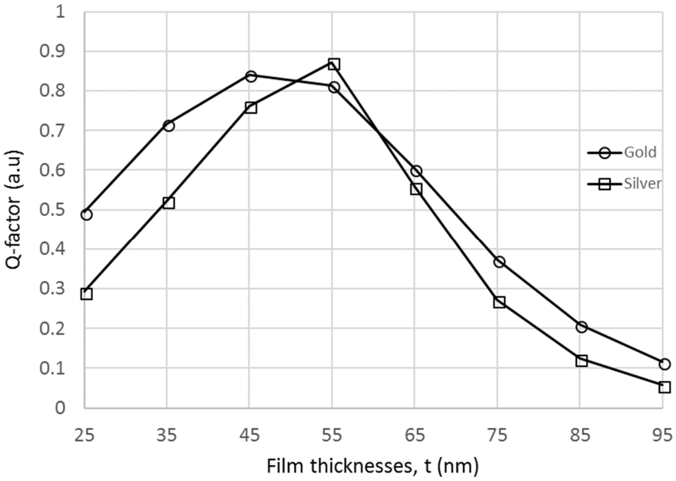


Fig. 5. Analysis of Q-factor represented by SPR curve depths for silver and gold with numerous thicknesses

Figure 6 shows the characteristics of SPP excitation by employing gold and silver at thickness t=55nm. Better SPR signal was achieved by coating the triangular prism with silver in which about 87.2% of incident light was successfully generated as SPP. Meanwhile, 81.4% of incident light was converted to SPP when gold thin film was introduced in the SPR setup. As discussed elsewhere, the only weakness of silver is due to its chemical degradation (i.e oxidization) when exposed to the moisture environment. To overcome this issue, the silver based-SPR sensor can be storage in dry inert atmosphere [35].

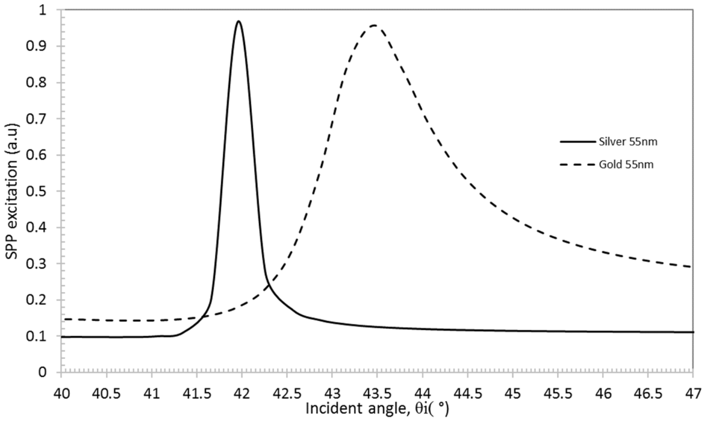


Fig. 6. SPP excitation between silver and gold at t=55nm

4. Conclusions

In conclusion, type of noble and its thicknesses mainly influenced the optimum generation of SPR. By omitting the oxidation issue, the employment of silver with thickness of t=55nm able to amplify the SPP excitation in comparison with gold. The analyses of Q-factor and FWHM are very important to justify the properties of SPR. We believe that the usage of silver to generate SPR will lead to the development of high sensitivity and low cost optical sensor.

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References

[1] Neethirajan, Suresh, and Digvir S. Jayas. "Nanotechnology for the food and bioprocessing industries." *Food and bioprocess technology* 4, no. 1 (2011): 39-47.

[2] Smolander, Maria, and Qasim Chaudhry. "Nanotechnologies in food packaging." *Nanotechnologies in food* 14, no. 2010 (2010): 86e-101e.

[3] Mahalik, Nitaigour P., and Arun N. Nambiar. "Trends in food packaging and manufacturing systems and technology." *Trends in food science & technology* 21, no. 3 (2010): 117-128.

[4] Smits, Edsger, Jeroen Schram, Matthijs Nagelkerke, Roel Kusters, Gert van Heck, Victor van Acht, Marc Koetse, Jeroen van den Brand, and G. Gerlinck. "Development of printed RFID sensor tags for smart food packaging." In *Proceedings of the 14th International Meeting on Chemical Sensors, Nuremberg, Germany*, pp. 20-23. 2012.

[5] Fuertes, Guillermo, Ismael Soto, Raúl Carrasco, Manuel Vargas, Jorge Sabattin, and Carolina Lagos. "Intelligent packaging systems: sensors and nanosensors to monitor food quality and safety." *Journal of Sensors* 2016 (2016).

[6] Puligundla, Pradeep, Junho Jung, and Sanghoon Ko. "Carbon dioxide sensors for intelligent food packaging applications." *Food Control* 25, no. 1 (2012): 328-333.

[7] Vargas-Sansalvador, I. M., Cormac Fay, Thomas Phelan, M. D. Fernández-Ramos, Luis Fermin Capitán-Vallvey, Dermot Diamond, and Fernando Benito-Lopez. "A new LED-LED portable CO2 gas sensor based on an interchangeable membrane system for industrial applications." *Analytica Chimica Acta* 699, no. 2 (2011): 216-222.

[8] Lin, Hsing-Ying, Chen-Han Huang, Jongmin Park, Divya Pathania, Cesar M. Castro, Alessio Fasano, Ralph Weissleder, and Hakho Lee. "Integrated magneto-chemical sensor for on-site food allergen detection." *ACS nano* 11, no. 10 (2017): 10062-10069.

[9] Ebarvia, Benilda S., and Isaiah E. Ubando. "Molecularly Imprinted Polymer Sensing Layer for Tetracycline Chemical Sensor Based on Piezoelectric Quartz Crystal Transducer." *Sensors & Transducers* 28 (2018): 7-11.

[10] Chen, Hai, Kai Zhou, and Guanghua Zhao. "Gold nanoparticles: From synthesis, properties to their potential application as colorimetric sensors in food safety screening." *Trends in Food Science & Technology* (2018).

[11] Park, Young Woo, Seong Min Kim, Jae Young Lee, and Wonhee Jang. "Application of biosensors in smart packaging." *Molecular & Cellular Toxicology* 11, no. 3 (2015): 277-285.

[12] Mukhtar, Wan Maisarah, Nur Auni Marzuki, and Affa Rozana Abdul Rashid. " Manipulating microbending losses in single mode optical fiber for pressure sensing." *Journal of Advanced Research in Applied Sciences and Engineering Technology* 9, no. 1 (2017): 14-21.

[13] Sarkar, Preetam, Shubham Subrot Panigrahi, Emily Roy, and Pratik Banerjee. "Nanosensors in food safety." Environmental Pollution 16 (2017): 185-207.

[14] Lang, Thomas, Thomas Hirsch, Christoph Fenzl, Fabian Brandl, and Otto S. Wolfbeis. "Surface plasmon resonance sensor for dissolved and gaseous carbon dioxide." *Analytical chemistry* 84, no. 21 (2012): 9085-9088.

[15] Narayanaswamy, Ramaier, and Otto S. Wolfbeis, eds. *Optical sensors: industrial environmental and diagnostic applications*. Vol. 1. Springer Science & Business Media, 2013.

[16] Mukhtar, Wan Maisarah, P. Susthitha Menon, and Sahbudin Shaari. "Effect of taper angle of the optical fiber microprobe in power collection." In *Advanced Materials Research*, vol. 403, pp. 3387-3391. Trans Tech Publications, 2012.

[17] Rashid, Affa Rozana Abdul, Amna Afiqah Nasution, Aisyah Hanim Suranin, Nur Athirah Taib, Wan Maisarah Mukhtar, Karsono Ahmad Dasuki, and Abang Annuar Ehsan. "Chemical tapering of polymer optical fiber." In *EPJ Web of Conferences*, vol. 162, p. 01015. EDP Sciences, 2017.

[18] Razak, Hanim Abdul, Nur Hidayah Sulaiman, Hazura Haroon, and Anis Suhaila Mohd Zain. "A fiber optic sensor based on Mach-Zehnder interferometer structure for food composition detection." *Microwave and Optical Technology Letters* 60, no. 4 (2018): 920-925.

[19] Nunes, Pedro S., Niels Asger Mortensen, Jörg P. Kutter, and Klaus B. Mogensen. "Refractive index sensor based on a 1D photonic crystal in a microfluidic channel." *Sensors* 10, no. 3 (2010): 2348-2358.

[20] Mukhtar, Wan Maisarah, Razman Mohd Halim, Karsono Ahmad Dasuki, Affa Rozana Abdul Rashid, and Nur Athirah Mohd Taib. "SPR sensor for detection of heavy metal ions: Manipulating the EM waves polarization modes." *Malaysian Journal of Fundamental and Applied Sciences* 13, no. 4 (2017): 619-622.

[21] Mukhtar, Wan Maisarah, Sahbudin Shaari, and P. Susthitha Menon. "Propagation of surface plasmon waves at metal thin film/air interface using modified optical waveguiding assembly." *Optoelectron Adv. Mat.* 7 (2013): 9-13.

[22] Novotny, Lukas, and Bert Hecht. *Principles of nano-optics*. Cambridge university press, 2012.

[23] Wu, L., H. S. Chu, W. S. Koh, and E. P. Li. "Highly sensitive graphene biosensors based on surface plasmon resonance." *Optics express* 18, no. 14 (2010): 14395-14400.

[24] Mukhtar, Wan Maisarah, Sahbudin Shaari, and P. Susthitha Menon. "Gold nanoparticles grown using modified seed-mediated growth technique." *Advanced Science Letters* 19, no. 5 (2013): 1412-1415.

[25] Grochowska, Katarzyna, Katarzyna Siuzdak, Jakub Karczewski, and Gerard Śliwiński. "Functionalization of indium-tin-oxide electrodes by laser-nanostructured gold thin films for biosensing applications." *Applied Surface Science*357 (2015): 1684-1691.

[26] Matsishin, M., A. Rachkov, A. Lopatynskyi, V. Chegel, A. Soldatkin, and A. El'skaya. "Selective amplification of SPR biosensor signal for recognition of rpoB gene fragments by use of gold nanoparticles modified by thiolated DNA." *Nanoscale research letters* 12, no. 1 (2017): 252.

[27] Samsuri, Nurul Diyanah, Wan Maisarah Mukhtar, Affa Rozana Abdul Rashid, Karsono Ahmad Dasuki, and Awangku Abdul Rahman Hj Awangku Yussuf. "Synthesis methods of gold nanoparticles for Localized Surface Plasmon Resonance (LSPR) sensor applications." In *EPJ Web of Conferences*, vol. 162, p. 01002. EDP Sciences, 2017.

[28] Mahmudin, Lufsyi, Edi Suharyadi, Agung Bambang Setio Utomo, and Kamsul Abraha. "Optical properties of silver nanoparticles for surface plasmon resonance (SPR)-based biosensor applications." *Journal of Modern Physics* 6, no. 08 (2015): 1071.

[29] Shah, Kruti, Navneet K. Sharma, and Vivek Sajal. "Analysis of fiber optic SPR sensor utilizing platinum based nanocomposites." *Optical and Quantum Electronics* 50, no. 6 (2018): 265.

[30] Murat, Noor Faezah, Wan Maisarah Mukhtar, Affa Rozana Abdul Rashid, Karsono Ahmad Dasuki, and Awangku Abdul Rahman Awangku Yussuf. "Optimization of gold thin films thicknesses in enhancing SPR response." In *Semiconductor Electronics (ICSE), 2016 IEEE International Conference on*, pp. 244-247. IEEE, 2016.

[31] Michel, David, Feng Xiao, and Kamal Alameh. "A compact, flexible fiber-optic Surface Plasmon Resonance sensor with changeable sensor chips." *Sensors and Actuators B: Chemical* 246 (2017): 258-261.

[32] Murat, Noor Faezah, Wan Maisarah Mukhtar, P. Susthitha Menon, Affa Rozana Abdul Rashid, Karsono Ahmad Dasuki, and Awangku Abdul Rahman Awangku Yussuf. "Influence of electromagnetic (EM) waves polarization modes on surface plasmon resonance." In *EPJ Web of Conferences*, vol. 162, p. 01008. EDP Sciences, 2017.

[33] Mukhtar, Wan Maisarah, Razman Mohd Halim, and Hazirah Hassan. "Optimization of SPR signals: Monitoring the physical structures and refractive indices of prisms." In *EPJ Web of Conferences*, vol. 162, p. 01001. EDP Sciences, 2017.

[34] Mukhtar, Wan Maisarah, Farah Hayati Ahmad, Nurul Diyanah Samsuri, and Noor Faezah Murat. "Study on plasmon absorption of hybrid Au-GO-GNP films for SPR sensing application." In *AIP Conference Proceedings*, vol. 1972, no. 1, p. 030007. AIP Publishing, 2018.

[35] Zhao, Jing, Shaoqing Cao, Changrui Liao, Ying Wang, Guanjun Wang, Xizhen Xu, Cailing Fu, Guiwen Xu, Jiarong Lian, and Yiping Wang. "Surface plasmon resonance refractive sensor based on silver-coated side-polished fiber." *Sensors and Actuators B: Chemical* 230 (2016): 206-211.